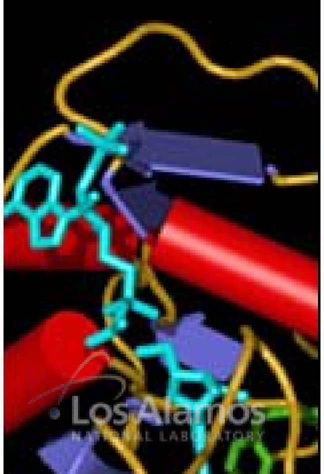
AOT & LANSCE The Pulse

October 2011

INSIDE



Daniel Shoemaker receives 23rd Rosen Prize

Daniel P. Shoemaker, a postdoctoral fellow at Argonne National Laboratory, is the winner of Los Alamos's 23rd Rosen Prize. The prize, established in honor of Louis Rosen, the father of LANSCE, is awarded for the most outstanding doctoral or master's thesis based on experimental or theoretical research performed at LANSCE. Criteria include the originality and scientific impact of the research and the student's contribution to the research.

Shoemaker was honored during the recent Rosenfest Lectures celebration, where he was among the speakers participating in the event. His doctoral-winning thesis, "Understanding Atomic Disorder in Polar and Magnetic Oxides," focused on creating and characterizing large-box models of materials that cannot be described using traditional crystallographic tools due to disorder on the nanoscale.

Shoemaker first came to the Lujan Center in 2007 as a user, then returned each year as a fellow of the University of California, Santa Barbara (UCSB)/Institute for Multiscale Materials Studies (IMMS). Anna Llobet and Thomas Proffen of the Lujan Center's Total Scattering team mentored him. His research, directed by Ram Seshadri (UCSB), used neutron total scattering to describe structure-property relations in disordered magnetic and functional oxides. Shoemaker received his doctorate from the Materials Department at UCSB. He defended his thesis in September 2010 and was awarded a Graduate Student Gold Award by the Materials Research Society in 2010.

First neutron diffraction study of a stoichiometric oxide compound of gold

Gold (Au)–traditionally regarded as one of the most inert elements in the periodic table–displays rich and various catalysis chemistries, much of which are still becoming known. Although the first report of carbon monoxide oxidation by gold was published in 1925, gold's catalytic action was noted in the 1820s during observations that it catalyzed the decomposition of ammonia. Due to gold's oxophobicity, its oxide crystal chemistry was relatively unknown until about 1960, and it was another decade until crystal structure refinements were reported for most of its ternary phases, and almost ten additional years before the crystal structure of the binary gold oxide, Au_2O_3, was determined.

continued on page 3

From Alex's Desk

Colleagues,

Let me take this opportunity to thank Alan Hurd for his 10 years of service to LANSCE and the Lujan Neutron Scattering Center; Alan has stepped away from his duties as Director of the Lujan Center to pursue the next phase of his career. The LANSCE community thanks him for his years of service to LANSCE and the Lujan Center. Please join us in bidding Alan farewell and best wishes in his future endeavors. In addition to the LANSCE-LC Center Leader opportunity (www.lanl.gov/orgs/hr/jobs/, Job Number: IRC1887 - R&D Manager 4) we are also searching for the LANSCE Protein Crystallography Station Leader (www.lanl.gov/orgs/hr/jobs/, Job Number: IRC1500-Science Scientist 4 -B-8/Bioenergy & Environmental Science). Search committees are in place for both opportunities; John Sarrao (sarrao@lanl.gov) and I (lacerda@lanl.gov) are the search committee chairs for the two positions respectively.

In response to the recent Office of Defense Programs long-term strategy for the construction of new experimental science facilities supporting NNSA missions, LANSCE is hosting a focused user meeting from January 8-10. The one-and-a-half day user meeting will allow the user community a means to affect this unique opportunity for significant improvements to the LANSCE scientific infrastructure. LANSCE is seeking user community input in three main topics:

- neutron sciences, including new directions in local structure research and neutron radiography capabilities;
- nuclear sciences, including plans to enhance capabilities to study a wide range of nuclear science experiments in the neutron energy range from approximately 1 keV to several MeV; and
- materials dynamics, where we are proposing to improve the proton radiography capability through an energy and current upgrade.

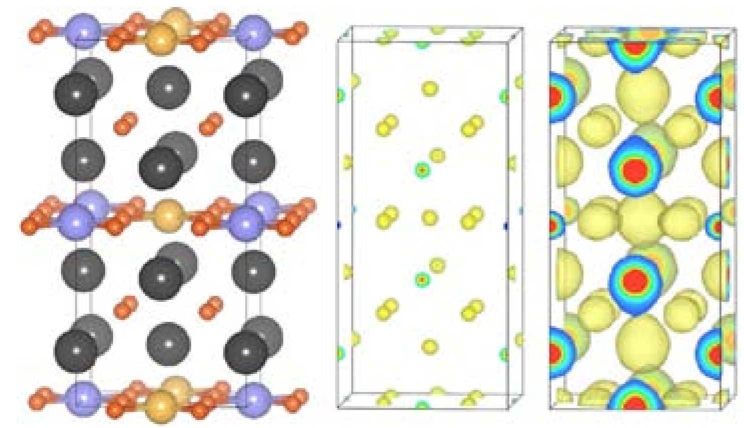
The workshop will facilitate user participation in helping LANSCE management prioritize future facility investments. For additional information and details, please see lansce.lanl.gov.

Last but not least, I would like to continue bringing to your attention the importance of TA-53 mesa traffic safety. I took part of an initiative organized by the TA-53 WSST where throughout the day we observed drivers along La Mesita road. The good news is a great number of drivers kept within the speed limit. Less good news, however, is that speeds exceeding 40mph were also measured and a lot of folks were still talking over the phone and driving. Please be aware of pedestrians along and crossing La Mesita. The marked pedestrian crossing south of Building-1 is still a major concern. Bottom line, please slow down and try to avoid the phone+driving combination.

LANSCE Deputy Division Leader Alex Lacerda

"In response to the recent Office of Defense Programs long-term strategy for the construction of new experimental science facilities supporting NNSA missions, LANSCE is hosting a focused user meeting... (to) allow the user community a means to affect this unique opportunity for significant improvements to the LANSCE scientific infrastructure."

Neutron... Anna Llobet (Lujan Center, LANSCE-LC) and University of California, Santa Barbara collaborators have reported the first neutron diffraction study of any stoichiometric oxide compound of gold (La_4LiAuO_8). A previous single crystal x-ray diffraction showed the compound to adopt an ordered modification of the Nd_2CuO_4 structure, containing two-dimensional sheets in which AuO_4 square planes are separated from one another by LiO_4 square planes. However, in light of the meager x-ray scattering factors of lithium and oxygen, relative to lanthanum and gold, the crystallographic description of this compound was questioned, and the possible catalytic role of Au^{+3} required further analysis. Given the very large atomic number differences between Au and O, neutron scattering is required to draw reliable conclusions with regard to Au^{3+}– O distances.



(Left) Unit cell depiction of La_4LiAuO_8. La is rendered black, Li blue, Au gold, and O orange. (Middle) Observed nuclear scattering densities (F_{obs}), shown at an isosurface level of ±0.3 fm $Å^{-3}$. (Right) X-N electron density isosurfaces at 1e$Å^{-3}$, determined by fixing the nuclear positions at those obtained from refinement of neutron data, and then reconstructed by the MEM/Rietveld method using synchrotron x-ray data.

In an excellent example of the strength of joint neutron and x-ray scattering techniques, Llobet and collaborators performed neutron and synchrotron x-ray powder diffraction experiments at the high intensity powder diffractometer (HIPD) instrument at the LANSCE Lujan Center and the Advanced Photon Source (Argonne National Laboratory) to examine the structure of La_4LiAuO_8. The team published the first neutron powder diffraction study of La_4LiAuO_8, definitively confirming the structure. X–N maps, which make use of nuclear positions obtained from Rietveld refinement of time-of-flight neutron diffraction data and electron densities obtained from synchrotron X-ray powder diffraction data, point to the highly covalent nature of the Au–O bonding in La_4LiAuO_8. This is in good agreement with charge densities and Bader charges obtained from full density functional relaxation calculations of the structure. The strength of the Au^{3+} stabilization is related to the raising of O 2p states by the highly electropositive La^{3+} and Li^+ counter cations, which enables improved orbital overlap between O 2p and Au 5d states. Researchers include J. A. Kurzman, S. L. Moffitt, and R. Seshadri (University of California, Santa Barbara); and A. Llobet (LANSCE-LC). Reference: "Neutron Diffraction Study of La_4LiAuO_8: Understanding Au^{3+} in an Oxide Environment, *Journal of Solid State Chemistry* **184**, 1439 (2011). The DOE Office of Basic Energy Sciences funded the Los Alamos portion of the research, which benefited from the use of the HIPD instrument at the Lujan Center. The work supports LANL's Materials for the Future science pillar.

Technical contact: Anna Llobet

Neutron scattering provides insight into enzymatic degradation of cellulose

Growing interest in alternative and renewable energy sources has brought increasing attention to the use of cellulose materials to produce fuels and useful chemicals. Conversion of cellulose typically involves three steps: pretreatment of the biomass, enzymatic hydrolysis of cellulose and hemicellulose to fermentable sugars, and fermentation of the sugars to liquid fuels or other products. Improving the efficiency of enzymatic hydrolysis of cellulose is one of the key technological hurdles to reduce the cost of producing ethanol and other transportation fuels from lignocellulosic material. A better understanding of how soluble enzymes (cellulases) interact with insoluble cellulose could aid the design of more efficient enzyme systems.

A multidisciplinary group of scientists used complementary techniques of neutron reflectivity (NR) and quartz crystal microbalance with dissipation monitoring (QCM-D) to examine the effect of cellulase enzymes on the structure of cellulose films. NR shows the profile of water through the film at nanometer resolution. It reveals whether an enzyme acts on the surface or throughout the bulk of the film and whether its activity results in removal of mass, increased water content, or changes in surface roughness. QCM-D provides changes in mass and film stiffness. The researchers used the Lujan Center time-of-flight surface profile analysis reflectometer (SPEAR) for the NR studies.

Comparison of cellulase action by a fungal enzyme extract with a single endoglucanase reveals important differences in the interactions of the enzymes with the films. The fungal enzyme extract initially digests cellulose at the surface, rapidly roughening the film/solution interface. Enzyme activity within the bulk of the film occurs after a significant fraction of the upper layer is degraded. On the same time scale, the single endoglucanase is active only at the surface. Because the fungal enzyme extract contains endoglucanases and exoglucanases, the scientists suggest that the interfacial roughening is due to the actions of the exoglucanases and possibly to the presence of cellulose

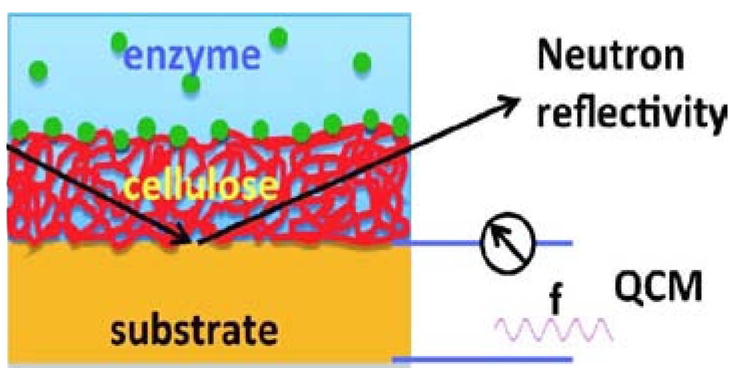
continued on page 4

Cellulose ... binding domains on the enzymes in the fungal extract. The single endoglucanase does not contain a cellulose binding domain.

Researchers include Michael Jablin, Manish Dubey, and Jaroslaw Majewski (LANSCE-LC); Gang Cheng, Ken Sale, Blake Simmons, Michael Kent (Joint BioEnergy Institute and Sandia National Laboratories); Zelin Liu, Chao Wang, and Alan R. Esker (Virginia Polytechnic Institute and State University); Jaclyn Murton (Sandia National Laboratories); Candice Halbert, James Browning, and John Ankner (Oak Ridge National Laboratory); and Bulent Akgun (National Institute of Standards and Technology and University of Maryland). Reference: "Neutron Reflectometry and QCM-D Study of the Interaction of Cellulases with Films of Amorphous Cellulose," *Biomacromolecules* **12**, 2216 (2011).

The DOE Office of Basic Energy Sciences, Scientific User Facilities Division sponsors research at the LANSCE Lujan Center. The work supports the Lab's Energy Security mission area and the Materials for the Future science pillar.

Technical contact: J. Majewski



Schematic of neutron reflectivity (NR) and quartz crystal microbalance with dissipation monitoring (QCM-D) of the interaction of a fungal enzyme extract (T. viride) and an endoglucanase from A. niger with amorphous cellulose films.

Neutron total scattering monitors shifts in valence states

The interplay between electronic, lattice, and magnetic degrees of freedom is at the origin of the broad variety of emergent phenomena exhibited by mixed metal oxides. Perovskites are a type of ionic crystal structure with the general formula ABX_3, where A is a tetravalent cation, B is a heptavalent cation, and X is an anion—usually oxygen, as in $NaNbO_3$ and $BaTiO_3$. Many of these compounds are ferroelectric. The group also includes some superconductors, semiconductors, and compounds that display magnetic ordering. Perovskite compounds containing manganese or ruthenium are among the most interesting of these systems because they possess many properties of technological importance such as colossal magnetoresistance, multiferroic behavior, itinerant electron ferromagnetism, and superconductivity in closely related Ruddlesden-Popper phases. (Ruddlesden-Popper phases are layered perovskites with the general formula $AO(ABO_3)n$.) The physical properties of perovskites, which contain both manganese (Mn) and ruthenium (Ru), are primarily governed by the oxidation states of the Mn and Ru cations. These cations often exist in a state of mixed valency. The properties of these materials can be tuned by controlling the ratio of Mn to Ru and by manipulating the charge and/or size of the cations on the A-site.

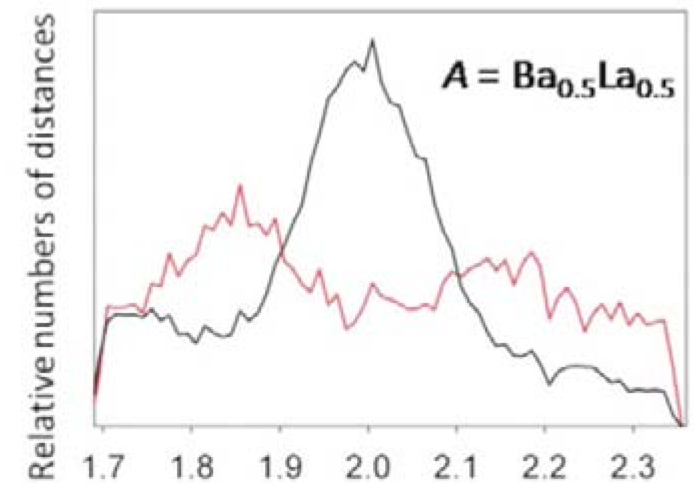
Lujan Center scientists Graham King and Anna Llobet (LANSCE-LC) and collaborators at The Ohio State University employed neutron scattering to monitor a shift in electron density between Mn and Ru cations in a series of $AMn_{0.5}Ru_{0.5}O_3$ perovskite compounds. In these compounds, the oxidation state of the Mn ions can vary between +3 and +4, and the oxidation state of the Ru ions can vary between +4 and +5. Since the Mn and Ru atoms are randomly distributed over the same crystallographic site, standard structure determination methods cannot distinguish between the coordination environments of the two atoms. The researchers used reverse Monte Carlo simulations, which involve large supercells containing approximately 10_4 atoms, to model the pair distribution functions of these materials. By modeling the distributions of Mn-O and Ru-O bond distances, the scientists showed that the relative concentrations of the various oxidation states of Mn and Ru depend on the size of the *A*-cation and that there is a shift in the *B*-site cation charge distribution from nearly equal amounts of Mn^{3+}, Ru^{5+}, Mn^{4+}, and Ru^{4+} for $SrMn_{0.5}Ru_{0.5}O_3$ to primarily Mn^{4+} and Ru^{4+} for $CaMn_{0.5}Ru_{0.5}O_3$. When smaller *A*-cations are used, the compounds reduce their concentrations of Mn^{3+} by shifting some of their electron density onto Ru. This study also found that the A-site cations lie closer to the Mn ions than to the Ru ions, and this asymmetry appears to be correlated to the degree of octahedral tilting.

Reference: "Linking Local Structure and Properties in Perovskites Containing Equal Concentrations of Manganese and Ruthenium," by Graham King, Rebecca A. Ricciardo, Jennifer R. Soliz, Patrick M. Woodward, and Anna Llobet, *Physical Review B* **83**, 134123 (2011). This work benefited from the use of the High-Intensity Powder Diffractometer (HIPD) at the Lujan Center and the Advanced Photon Source at Argonne National Laboratory, which the DOE, Office of Science support. The work supports the Laboratory's Energy Security mission area and the Materials of the Future capability.

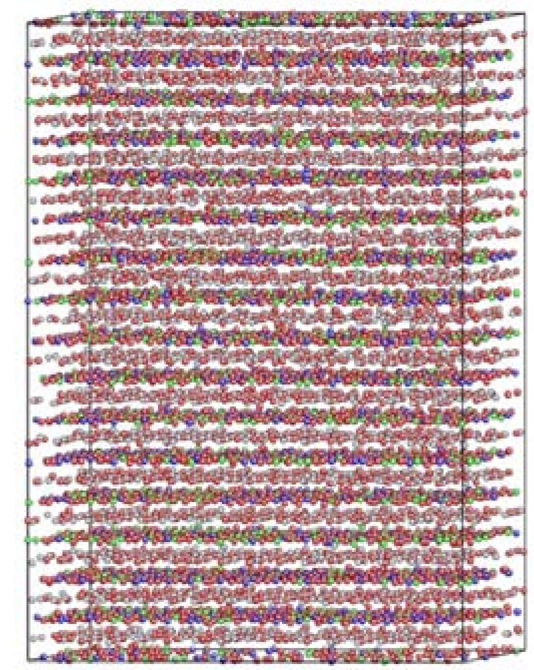
Technical contact: Anna Llobet

continued on page 5

Neutron ...



Above: Distribution of Mn-O (red) and Ru-O (black) bond lengths in $BaLaMnRuO_6$. Below: Reverse Monte Carlo supercell of Sr_2MnRuO_6, which contains 10,240 atoms.



Neutron reflectometry examines the performance of radiation-resistant materials

Precipitation of implanted helium (He) is a major concern for the performance and survivability of plasma-facing components in future nuclear fusion reactors. The deleterious effects of He may be minimized if it can be trapped at special microstructural features. LANL scientists and collaborators investigated metallic copper/niobium (Cu/Nb) multilayers and discovered that a remarkably high concentration of He can be trapped at certain heterophase interfaces before nanometer-scale bubbles are resolved via transmission electron microscopy (TEM). Atomistic modeling suggests that excess atomic volume leads to a high He "solubility" at these interfaces. Because TEM cannot resolve He clusters smaller than 1-2 nm in diameter, other techniques are needed to characterize He concentration profiles across interfaces.

An interdisciplinary group of scientists used neutron reflectometry (NR) to determine the changes in the transverse chemical profile of Cu/Nb layered nanocomposites due to He ion migration, absorption, and storage after ion implantation. The researchers performed the NR experiments on the surface profile analysis reflectometer (SPEAR) at the Los Alamos Neutron Science Center. NR involves the specular reflection of a neutron beam from a surface or film and provides sub-angstrom level resolution in location of the He-enriched interfaces. NR provides a nuclear (chemical) scattering length density (NSLD) depth profile of the sample with Angstrom resolution averaged over the coherent area of the neutron beam on the sample surface – typically microns^2. NSLD is the product of the number density of atoms and their nuclear coherent scattering lengths. From NR measurements, layer parameters such as thickness, density, chemical composition, and interface and surface roughnesses can be determined with sub-angstrom precision regardless of the crystallinity of the sample. Neutron scattering is a unique tool to study such nanolayered composites because the scattering strength is a non-monotonic function of the Z number of a material. Therefore, elements like Cu and Nb provide the necessary neutron scattering contrast even though their x-ray scattering contrast is low. Additionally, unlike electron microscopy, which yields local structure information, NR provides data averaged over a large sample area.

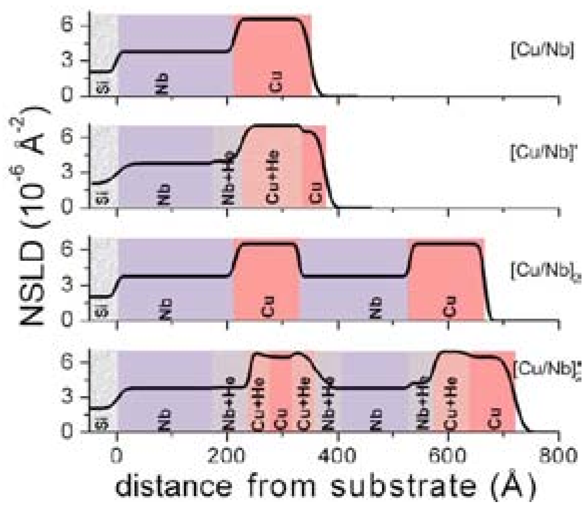
Neutron reflectometry characterized [Cu/Nb]x layered nanocomposites that had been exposed to extreme helium ion doses at the Ion Beam Materials Laboratory. Measurement of the effects of He ions on the interfacial roughness, layer swelling, and chemical mixing revealed that regions of high He concentration localize at Cu/Nb interfaces while bulk Cu and Nb layers remain intact (see figure). The interfaces in [Cu/Nb]x systems irradiated with high He ion doses absorbed and stored He without distorting the planar structure of the layers. Due to the He irradiation, the Cu/Nb interfacial regions broadened approximately ten-fold, and most of the He ions were segregated into these regions, swelling both the Cu and Nb layers. The scientists attribute this remarkable behavior to the efficient trapping and storage of He at interfaces as compared to bulk. Analysis of NR data from these samples provides insight into the behavior of interfaces in layered nanocomposites under an extreme environment, such as may be expected in the first wall of a fusion reactor.

Researchers include Mikhail Zhernenkov, Michael Jablin, and Jaroslaw Majewski (LANSCE-LC); Amit Misra, Michael Nastasi,

continued on page 6

Materials . . . and Jon K. Baldwin (Center for Integrated Nanotechnologies, MPA-CINT); Yongqiang Wang (Structure/Property Relations, MST-8); and Michael Demkowicz (Massachusetts Institute of Technology). Reference: "Trapping of Implanted He at Cu/Nb Interfaces Measured by Neutron Reflectometry," *Applied Physics Letters*, in press. The research benefited from the use of the Lujan Neutron Scattering Center at LANSCE funded by the DOE Office of Basic Energy Sciences. LANL's Laboratory Directed Research and Development (LDRD) program sponsors the work on He ion implantation in multilayers. The research supports the Lab's Energy Security mission area and the Materials for the Future science pillar.

Technical contact: J. Majewski



Nuclear scattering length density (NSLD) profiles obtained from the neutron reflectivity (NR) fits and schematics of the real-space interpretations used to model the experimental data. A prime after a sample name indicates that the curve corresponds to a measurement after He ion implantation.

Measuring the fission neutron spectrum at LANSCE

Scientists from LANL, Japan (Kyushu University), and France (CEA Bruyères-le-Châtel) have measured the energy distribution of neutrons from neutron-induced fission. The data are used as constraints in the Los Alamos model of nuclear fission to obtain information on the total kinetic energy of the fission fragments. Moreover, the data will improve the evaluated data libraries, which are used in applications to nuclear energy, criticality safety, and nuclear weapons development.

A nucleus of uranium, plutonium, or certain other elements can be induced to fission, or split into two lighter nuclei, by the addition of a neutron. When fission occurs, the two fission fragments can emit energetic neutrons, which then can induce further fissions. This is the principle of the chain reaction. For reactors, the chain reaches a steady state, whereas for weapons and other super-critical systems, the number of fissions increases exponentially with time. Because the probability of fission depends on the neutron energy, the energy spectra of the neutrons from fission must be known in order to calculate the neutron multiplication of a fissionable system. Although several measurements have been made of the neutron emission spectrum from fission induced by thermal neutrons (neutron energy distribution characteristic of room temperature), very few measurements have been performed for fission induced by fast neutrons (neutrons with a kinetic energy in excess of 0.1 MeV). The two measurements for the important isotope plutonium-239 (^{239}Pu), are inconsistent. Therefore, the researchers' goal in the measurements at the Weapons Nuclear Research (WNR) facility at LANSCE is to make significant improvements in these basic data.

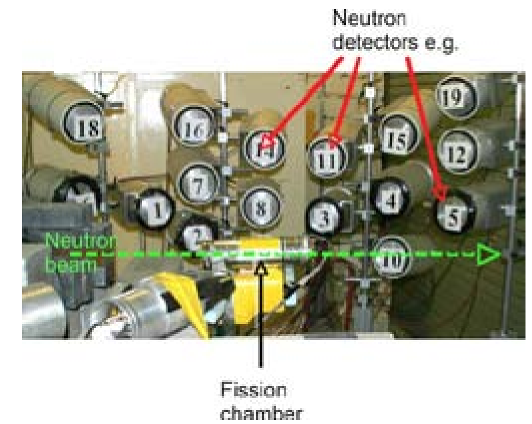
The approach uses a double time-of-flight technique. The WNR neutron source is pulsed to give the "start" signal, and the time of flight of neutrons to the fission detector located 22.7 meters away gives the energy of the neutron inducing the fission. An electronic pulse created when fission takes place is the "stop" signal for the timing. The fission pulse is also used as the "start" signal to time neutrons from fission in the fission chamber to neutron detectors placed 1 meter away. These detectors are called the FIGARO (Fast Neutron-Induced Gamma-Ray Observer) array. By collecting data from many fission events, a distribution of the energies of the fission neutrons is obtained and can be compared with predictions of the Los Alamos Model. The fission chamber, which was supplied by the French colleagues, and the neutron detectors are pictured in the photo. Samples of the results, shown in the figure, are compared with data in the Evaluated Neutron Data File, ENDF/B-VII.0, which is used around the world for applied calculations, and with predictions of the revised Los Alamos Model. Their results are in agreement with the data in ENDF/B-VII.0. Scientists are continuing the work to reduce the size of the error bars and to extend the measurements to neutrons with energies below 1 MeV. The work supports the Lab's Nuclear Deterrence and Energy Security mission areas and the Science of Signatures and Materials for the Future science capabilities.

Scientists participating in the research include Shusaku Noda [Kyushu University, Neutron Science (LANSCE-NS), and Nuclear and Particle Physics, Astrophysics and Cosmology (T-2)], Robert Haight, Ronald Nelson, Matthew Devlin, and John O'Donnell (LANSCE-NS); Audrey Chatillon, Thierry Granier, Gilbert Belier, and Julien Taieb (CEA); Toshihiko Kawano and Patrick Talou (T-2). Reference: "Measurement and Analysis of Prompt Fission Neutron Spectra from 1 to 8 MeV in Neutron-induced Fission of ^{235}U and ^{239}Pu Using the Double Time-of-flight Technique," P*hysical Review C* **83**, 034604 (2011).

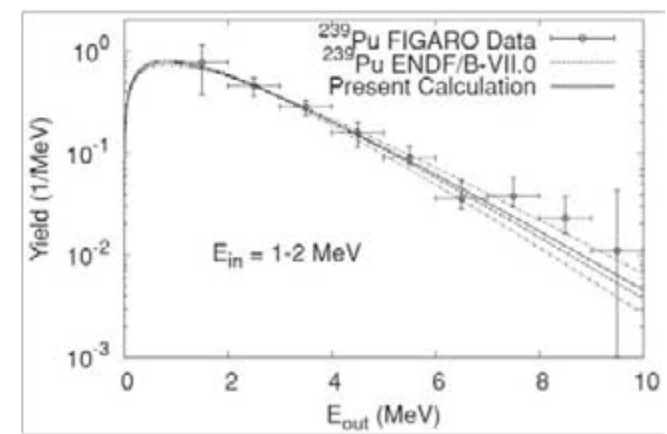
Technical contact: B. Haight

continued on page 7

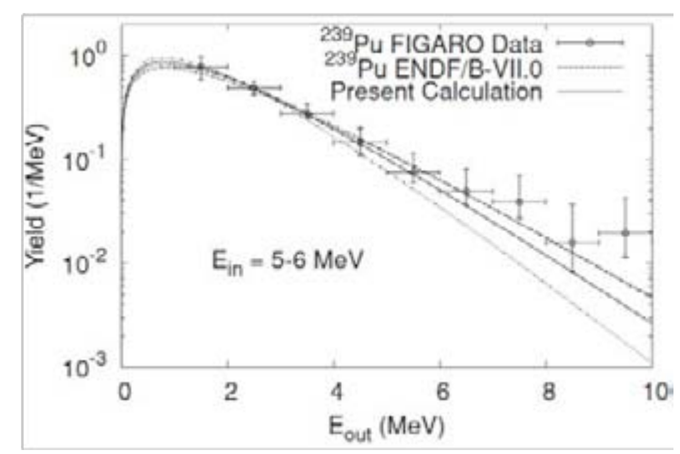
Fission . . .



Fission chamber and neutron detectors (numbered).



Sample results of the prompt fission neutron spectra for two incident neutron energies, 1-2 MeV and 5-6 MeV. The data (FIGARO) are compared with those in the Evaluated Nuclear Data Library (ENDF) and with predictions of the modified the Los Alamos Model (present calculation). Scientists adjusted input parameters of the latter to fit the present data.



Celebrating service

Congratulations to the following AOT and LANSCE employees celebrating service anniversaries this month:

Rex Hjelm, LANSCE-LC	25 years
Peter Olivas, AOT-IC	25 years
Ray Roybal, AOT-MDE	15 years
Ernest Geros, AOT-ABS	10 years
Andrew Jason, AOT-ABS	5 years
Michal Mocko, LANSCE-LC	5 years

HeadsUP!

Seasonal flu vaccine available through local pharmacies

Present your LANS Blue Cross Blue Shield card

The 2011 seasonal flu vaccine is available now from area pharmacies, clinics, and personal medical providers. LANS employees can receive the seasonal vaccine from many local providers and pharmacies without a co-pay by presenting their Blue Cross Blue Shield of New Mexico health plan card. Employees should call ahead to check hours and availability. Occupational Medicine will not be providing the flu vaccine onsite except for those LANL workers who receive the flu vaccine as part of their medical surveillance program.

In addition, the seasonal flu vaccine will be available free of charge at many community health fairs between now and the end of October. A list of locations in New Mexico contracted by Blue Cross Blue Shield of New Mexico to provide the seasonal flu vaccine at no out-of-pocket charge to individuals covered by the BCBS health plan is at http://int.lanl.gov/news/newsbulletin/pdf/vaccine_network_list_092810.pdf. Employees are encouraged to call pharmacies first to find out what times the flu vaccine will be offered.

Winter closure information

An all-employee memo about LANL's 2011 winter closure was issued by Associate Director for Business Services Mark Barth. Read the memo at int.lanl.gov/memos/2011/09/LANL-ALL2447.pdf for more information.

AOT & LANSCE The Pulse

Published monthly by
the Experimental Physical Sciences Directorate.
To submit news items or for more information,
contact Karen Kippen,
EPS Communications,
at 606-1822, or kkippen@lanl.gov
LALP-11-017
To read past issues see
http://int.lanl.gov/orgs/lansce/The_Pulse/index.shtml

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by Los Alamos National Security, LLC, for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396.